Emission Sources and Formation of Particulate Organic Matter (POM)

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A summary of observations from 1 airborne and 2 ship-based measurement campaigns in New England
## Sources of Particulate Organic Matter (POM)

### Direct Emissions

<table>
<thead>
<tr>
<th>Source</th>
<th>Amount (Tg y(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass burning</td>
<td>43.7</td>
</tr>
<tr>
<td>Fossil Fuel combustion</td>
<td>3.2</td>
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</table>

### Secondary Formation

<table>
<thead>
<tr>
<th>Compound</th>
<th>Amount (Tg y(^{-1}))</th>
<th>Yield (%)</th>
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<tbody>
<tr>
<td>Monoterpenes</td>
<td>130</td>
<td>14%</td>
</tr>
<tr>
<td>Isoprene</td>
<td>500</td>
<td>0.9-3.0%</td>
</tr>
<tr>
<td>Toluene</td>
<td>6.7</td>
<td>11%</td>
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**Bottom line:**
- Direct emissions > secondary formation
- Most POM contains modern carbon
Our Observations in New England

1. POM was associated with urban emissions
2. POM was mostly secondary
3. Formation could not be explained from known precursors
1. Mass loading of POM correlates well with urban pollutants
Iso-propyl nitrate is an oxidation product from propane and other mainly anthropogenic hydrocarbons (de Gouw, JGR 2005)
POM / WSOC vs. CO During ICARTT 2004

Ron Brown AMS data (Quinn and Bates)

WP-3D WSOC data excluding forest fire plumes (Sullivan, JGR in press)
No Obvious Correlation with Biogenic Emissions

Ron Brown AMS data from NEAQS 2002
POM correlates better with fossil-fuel related emissions

\[ \iff \text{inconsistent with C14 data that says carbon is modern?} \]
2. Direct, urban emission sources of POM are relatively small on regional scales
Direct, Urban Emissions of POM

AMS data from NEAQS 2002

Minor POM enhancements close to urban sources
POM emissions from vehicles

$\Delta \text{POC}/\Delta \text{CO} = 2.1 \, \mu \text{g m}^{-3} \, \text{ppmv}^{-1}$
(Kirchstetter, AE 1999)

$\Delta \text{toluene}/\Delta \text{CO} = 4.2 \, \text{ppbv ppmv}^{-1}$
(Warneke, JGR in press)

$\Delta \text{POM}/\Delta \text{POC} = 1.78$
(de Gouw, JGR 2005)

From which follows:

$\Delta \text{POM}/\Delta \text{toluene} = 0.9 \, \mu \text{g m}^{-3} \, \text{ppbv}^{-1}$

$\Delta \text{toluene} = 0.6 \, \text{ppbv}$  \Rightarrow  $\Delta \text{POM} = 0.5 \, \mu \text{g m}^{-3}$
3. Mass loading of POM in urban plumes increases strongly in first 24 hours
WSOC Growth in NYC plume

WP-3D data from ICARTT

ΔWSOC/ΔCO:

8.9 µg m⁻³ ppmv⁻¹ (July 20)

23 µg m⁻³ ppmv⁻¹ (July 21)

N.B. ΔOC/ΔCO:

2.1 µg m⁻³ ppmv⁻¹ (tunnel study)
WSOC Growth in Urban Plumes

- Transport age from Flexpart or trajectories
- Photochemical age from benzene/toluene ratios

WP-3D data from ICARTT
4. Increase in POM cannot be explained by removal of commonly measured VOCs
Secondary Formation from Measured VOCs

- Sums up to ~3.7 $\mu$g m$^{-3}$ ppmv$^{-1}$
- Toluene ~46% of the secondary formation
Secondary formation from measured VOCs cannot explain the observed increase in POM
What Does it Mean?
Possible Explanations for the Discrepancy?

1. Formation from higher-mass VOCs?
   *Donahue, ES&T 2006*
   Only few measurements. Enough mass available?

2. Formation more efficient than observed in smog chambers?
   20% yield for all VOCs explains data

3. Formation from biogenic VOCs more efficient in urban air?
   Would explain correlation with pollutants
   Would explain the C14 data
   Biogenic precursors ≠ naturally occurring POM

Similar observations:

*Heald, GRL 2005*  *ACE-Asia*
*Takegawa, GRL 2006*  *Tokyo*
*Volkamer, GRL 2006*  *Mexico City*
## Sources of POM: A Revision

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<thead>
<tr>
<th>Source</th>
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<th>Yield (%)</th>
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\(^{a}\) Assuming:
1. A global CO source of 450 Tg y\(^{-1}\)
2. Secondary formation of 30 \(\mu g C m^{-3} (ppmv CO)^{-1}\)

**Bottom line:** Secondary formation from urban emissions may be much higher than previously recognized.
Acknowledgements

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